

REMOVAL OF ARSENIC FROM GROUNDWATER BY IRON OXIDE-COATED SAND : DEVELOPMENT OF A HOME ARSENIC REMOVAL UNIT

**A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of**

MASTER OF TECHNOLOGY

by

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to the

**DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR**

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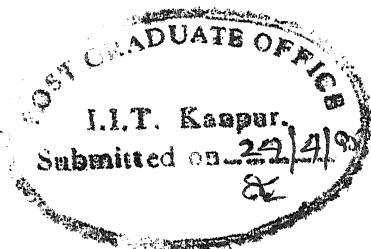
CERTIFICATE

Certified that the work presented in this thesis entitled "Removal of Arsenic from Groundwater by Iron Oxide-Coated Sand : Development of a Home Arsenic Removal Unit" by Captain Arun Joshi has been carried out under my supervision and has not been submitted elsewhere for a degree.

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TABLE OF CONTENTS

	Page
1. INTRODUCTION	1
2. BACKGROUND INFORMATION	4
2.1 Arsenic : Its Occurrence and Effects	4
2.1.1 Sources	4
2.1.2 Mode of Occurrence of Arsenic	5
2.1.3 Health Effects	6
2.1.4 Guidelines for Drinking Water Quality	7
2.2 Removal of Arsenic from Water	8
2.3 Iron Oxide-Coated Sand - An Adsorptive Filtration Medium	11
3. SCOPE OF THE PRESENT STUDY	14
4. MATERIALS AND METHODS	16
4.1 Arsenic-Bearing Water	16
4.2 Determination of Arsenic	16
4.3 Preparation of Iron Oxide-Coated Sand	19
4.4 Arsenic Sorption Kinetic Test	22
4.5 Column Test	22
5. RESULTS AND DISCUSSION	25
5.1 Arsenic Sorption Kinetic Test	25
5.2 Column Test	25
6. HOME ARSENIC REMOVAL UNIT	32
7. SUMMARY AND SUGGESTIONS	36
REFERENCES	38

LIST OF TABLES

Number	Title	Page
1	Analysis of I.I.T., Kanpur Tap Water	16
2	Column loading-regeneration material balance for arsenic (III)	29
3	Column loading-regeneration material balance for arsenic (V)	30

LIST OF FIGURES

Number	Title	Page
1	Calibration curve for arsenic (III)	20
2	Calibration curve for arsenic (V)	21
3	Kinetics of arsenic sorption on uncoated and iron oxide-coated sand	25
4	Performance of iron oxide-coated sand in arsenic (III) removal in ten cycles of column test	27
5	Performance of iron oxide-coated sand in arsenic (V) removal in ten cycles of column test	28
6	Home arsenic removal unit	33
7	Performance of home arsenic removal unit	34

1. INTRODUCTION

Water-related diseases/ailments constitute a major proportion of the public health problems in developing countries. Any improvement in water quality has a positive effect on the well-being of the society as a whole. By no means, this is a challenging task and in developing countries, the major obstacles in achieving this goal are the constraints of funds and skilled manpower. Since economic considerations do not permit community water treatment plants in rural areas, most developing countries are resorting to groundwater supplies which are usually free from microbiological contaminants and may be supplied as drinking water without much treatment. However, in specific locations, groundwater supplies may be contaminated with toxic chemicals which may cause adverse health effects after prolonged periods of exposure and efforts must be made to minimise them. Of particular concern are contaminants that have cumulative toxic properties, such as heavy metals and substances that are carcinogenic (WHO, 1993). Inorganic arsenic is a documented human carcinogen and with a view to reducing the concentration of this carcinogenic contaminant in drinking water, a provisional guideline value for arsenic in drinking water of 0.01 mg/L has been established (WHO, 1993).

Arsenic is an ubiquitous element with metalloid properties. In nature, it is widely distributed in a number of minerals, mainly as the arsenides of copper, nickel and iron or as arsenic sulfide or oxide. Arsenic contamination of groundwater can result from leaching of man-made toxic arsenic compounds or

from natural dissolution of minerals from the subterranean strata. High arsenic levels in groundwater were reported from many parts of the world which include Taiwan (Kuo, 1968; Shen, 1973), Japan (Terada, 1960), China (Tseng, 1968), Chile (Borgono et al., 1977), and USA (Bellack, 1971; Hathway and Rubel, 1987).

In India, the first case of arsenic poisoning was reported from a few villages in the northern parts of the country (Datta and Kaul, 1976). With reports of arsenical dermatosis in six districts of West Bengal, the problem assumed further significance. High levels of arsenic in the tubewell water in these areas of West Bengal were linked to arsenical dermatosis and skin cancer (Chakraborty and Saha, 1987). A detailed analysis of the water samples from six villages of the five districts of West Bengal revealed that the arsenic content of the tubewell water was as high as 0.2-2.0 mg/L (Chakraborty and Saha, 1987).

Methods for removal of arsenic from water include iron or alum coagulation, filtration, reverse osmosis, ion exchange and adsorption by activated alumina, and have been applied with varying degrees of success in the field. However, these methods cannot be applied in the rural areas of developing countries due to their high cost and requirement of skilled maintenance. Thus, there is an urgent need to develop simple, low-cost alternatives for arsenic removal for use in such areas. Excellent removal of arsenic (V) on Fe^{2+} -treated activated carbon has been reported (Huang and Vane, 1989). Effective removal of arsenic (III) and arsenic (V) by chelating resins in the ferric iron form has also

been observed (Chanda et al., 1988). Further, adsorptive filtration by iron oxide-coated sand, a novel method which combines the advantages of adsorption and filtration, has been proposed by Edwards and Benjamin (1989a) for removal/recovery of heavy metals from metal-bearing wastewaters. In laboratory tests, the method has been found useful in removing metals such as copper, chromium, cadmium, lead, and nickel from synthetic waste solutions (Benjamin and Sletten, 1992; Edwards and Benjamin, 1989b), zinc from a treated metal-bearing waste (Benjamin and Sletten, 1992), and cadmium and cyanide from a metal-plating waste (Satpathy, 1993). The Inorganic Contaminants Research Committee of the American Water Works Association has identified studies on the possible removal of arsenic using iron oxide-coated sand in fixed-bed columns as one of the current research needs (Committee Report, 1993).

The present study was undertaken to assess the suitability of iron oxide-coated sand for removal of arsenic from groundwater *vis-à-vis* its use as a medium in home arsenic removal units in rural areas of developing countries.

2. BACKGROUND INFORMATION

This chapter is aimed at providing a background for the study — occurrence and effects of arsenic, methods for arsenic removal from water, and iron oxide-coated sand as an adsorptive filtration medium.

2.1 Arsenic : Its Occurrence and Effects

2.1.1 Sources

There is no one distinct source of arsenic in the environment, and it is naturally distributed throughout the earth's biosphere, and can be found just about anywhere. Arsenic occurs ubiquitously in nature and is usually present in the form of compounds with sulfur and with many metals (copper, cobalt, iron, lead, zinc, etc.); the average concentration in the earth's crust is about 2 mg/kg. Oceans are also great reservoirs of arsenic with concentration approximately 14 T/m^3 (Wenk, 1969). Deep sea sediments have been found to have an arsenic concentration ranging from a few ppm to as much as 455 ppm with the highest in areas where active oceanic ridges are present (Gulledge and O'Connor, 1973). Common mineral forms of arsenic compounds are arsenopyrite ($\text{FeS}_2 \cdot \text{FeAs}_2$), realgar (AsS), and orpiment (As_2S_3) (Hurlbut, 1968). Methylated arsenic compounds occur due to biological activities. In seawater, some marine organisms transform inorganic arsenic into more complex organic compounds like arsenobetaine, arsenochlorine, and arsoniumphospholipids (WHO, 1981).

In some localized geographical areas, commercial use and production of arsenic compounds have resulted in significant elevation in the amount of environmental arsenic above natural background levels. Arsenic compounds are mainly used in agriculture and forestry as pesticides, herbicides and silvicides. Arsenic trioxide, lead arsenate and calcium arsenate are used as insecticides and are highly toxic (Gulledge and O'Connor, 1973; Woodward, 1960). Other industrial applications of arsenic compounds include utilization as weed killers, rodenticides, wood preservatives, decolorizers in glass manufacturing, formulation of pigments, and manufacture of lead shots (Browning, 1969).

2.1.2 Mode of Occurrence of Arsenic

Arsenic is a commonly occurring toxic element, which occurs in both organic and inorganic forms (Braman and Foreback, 1973; Crecelius, 1974) but the organic arsenic species are generally present in smaller amount than the inorganic forms, arsenite (arsenic (III), trivalent), and arsenate (arsenic (V), pentavalent). Among inorganic compounds, arsenic trioxide or arsenous oxide (As_2O_3 or As_4O_6), arsenic pentoxide (As_2O_5), arsenous acid (H_3AsO_3), arsenious acid (HAsO_2), arsenites (salts of arsenous acid) (H_2AsO_3^- , HAsO_3^{2-} or AsO_3^{3-}), arsenates (salts of arsenious acid) (AsO_2^-), arsenic acid (H_3AsO_4), arsenates (salts of arsenic acid) (H_2AsO_4^- , HAsO_4^{2-} or AsO_4^{3-}), arsenic sulfide (As_2S_3) are important (WHO, 1981).

Data on the speciation of arsenic-bearing groundwaters is relatively scarce; however, it is known that the valence state of arsenic in groundwater varies with location. Inorganic arsenic may occur totally as arsenite, as arsenate or any mixture of these two valence states. The speciation of arsenic is important because arsenite form is considered to be more toxic than the arsenate form. In natural water, arsenite is ultimately oxidized to arsenate in the presence of dissolved oxygen (O'Connor, 1974).

✓ Sodium arsenite (NaAsO_2) is the most frequently used form of arsenic. When sodium arsenite is added to water with a pH less than 9.5, the predominant aqueous form is arsenious acid (HAsO_2). If the solution pH is greater than 9.5, arsenite (AsO_2^-) is the predominant species. The other species of arsenic that is commonly found in water is the arsenate ion (AsO_4^{3-}), which is not so toxic, as arsenite (Gulledge and O'Connor, 1973).

In a system including oxygen and sulfur, Ferguson and Gavis (1972) showed that the soluble arsenite species are H_3AsO_3 , H_2AsO_3^- , and HAsO_3^{2-} . The soluble arsenate species are H_3AsO_4 , H_2AsO_4^- , HASO_4^{2-} , and AsO_4^{3-} . In the pH range 4-10, the predominant arsenite form is H_3AsO_3 and the predominant arsenate species are H_2AsO_4^- and HASO_4^{2-} (Ferguson and Gavis, 1972).

2.1.3 Health Effects

Arsenic compounds are known for their toxicity to man as both poisons and carcinogenic agents. The toxicity of arsenic compounds depends on the chemical and physical form of the

compound, the amount of ingestion, term of exposure, dietary levels of interacting elements, and the age and sex of the exposed individual. Inorganic arsenic is more toxic than organic arsenic; trivalent inorganic arsenic is more hazardous than the pentavalent form.

Acute effects caused by ingestion of inorganic arsenic compounds are very well documented in the literature. Long term exposure to low concentrations may cause acute and sub-acute effects on various parts of the body. Acute effects include gastrointestinal damage resulting in severe vomiting and diarrhoea, often with blood tinged stools, muscular cramps, facial oedema, and cardiac abnormalities. Sub-acute effects mainly involve the respiratory, gastrointestinal, cardiovascular, nervous, and haematopoietic systems (Gulledge and O'Connor, 1973).

A relatively high incidence of skin and possibly other cancers that increase with dose and age has been observed in populations ingesting water containing high concentrations of arsenic (WHO, 1973). Chen and Wu (1962) reported high incidence of skin cancer in Taiwan after consumption of water containing more than 0.3 mg/L arsenic. Tseng et al. (1961) also observed association of skin cancer with drinking wellwater containing 0.5 mg/L arsenic.

2.1.4 Guidelines for Drinking Water Quality

Data on the association between internal cancers and ingestion of arsenic in drinking water were insufficient for

quantitative assessment of risk. Instead, owing to the documented carcinogenicity of arsenic in drinking water in human populations, the lifetime risk of skin cancer was estimated using a multistage model. On the basis of observations in a population ingesting arsenic-contaminated water, the concentration associated with an excess lifetime skin cancer risk of 10^{-5} was calculated to be 0.17 $\mu\text{g/L}$. This value may, however, overestimate the actual risk of skin cancer owing to the possible contribution of other factors to disease incidence in the population and to possible dose-dependent variations in the metabolism that could not be taken into consideration. In addition, this value is below the practical quantification limit of 10 $\mu\text{g/L}$. With a view to reducing the concentration of this carcinogenic contaminant in drinking water, a provisional guideline value for arsenic in drinking water of 0.01 mg/L is established (WHO, 1993). The estimated excess lifetime skin cancer risk associated with exposure to this concentration is 6×10^{-4} .

2.2 Removal of Arsenic from Water

Many methods have been used for the removal of arsenic from water, under both laboratory and field conditions. Adsorption-coprecipitation with hydrolyzing metals such as aluminium and iron (III) are used most commonly for removing arsenic. Iron salts appear to be more effective than those of aluminium in this type of treatment. Precipitation with sulfide, and adsorption on activated carbon and alumina may also be used

for removing arsenic. Ion exchange and reverse osmosis have been tried on a limited basis.

It has been reported that effluent arsenic levels of 0.05 mg/L are obtainable by precipitation of arsenic as the sulfide, with addition of sodium or hydrogen sulfide at pH 6-7 (Curry, 1972). Sulfide precipitation has been found effective for arsenate, but ineffective for arsenite; ferrous sulfate precipitation is also active in removing arsenate only, whereas lime is effective on both arsenite and arsenate wastestreams, since arsenite converts to the pentavalent form at high pH (Rosehart and Lee, 1972). Dutta and Chaudhuri (1991) investigated lime softening with powdered bituminous coal additive for possible enhancement of arsenic removal from a groundwater (total arsenic 0.68-0.70 mg/L; arsenic (III) 0.59-0.60 mg/L). Residual arsenic level below the 1984 WHO guideline value for arsenic (0.05 mg/L) was achieved at a lime dose of 800 mg/L (pH 11.5) with 2 g/L powdered coal additive.

Conventional water treatment involving coagulation, settling and filtration also yielded a significant removal of arsenic with the use of ferric sulfate as coagulant (Buswell et al., 1943). Pilot plant study by Logsdon et al. (1974) showed 91-94% and 75-79% removal of arsenates by ferric sulfate and alum, respectively. Dual-media filtration achieved an additional 5-7% removal in both the cases. However, arsenite removals of only 10-25% were achieved by alum and 40-60% by ferric chloride. Oxidation of arsenite to arsenates by chlorination prior to

coagulation yielded same results as arsenate. Similar results of arsenate removal were also reported by Gullledge and O'Connor (1973).

Shen (1973) performed full-scale treatment of deepwell water to remove arsenic. The treatment involved coagulation and sedimentation followed by slow sand filtration. Chlorine was found to be more effective oxidant than potassium permanganate. Ferric chloride served as the best coagulant as compared to alum, copper sulfate and ferrous sulfate. He also studied arsenic removal using special ion-exchanger and concluded that removal of arsenic from water was good but was too costly and complex. Treatment using alumina with proper pH adjustment and treatment using charcoal are also feasible removal techniques for arsenic (Bellack, 1971; Hathway and Rubel, 1987).

The mechanism of coprecipitation is the probable explanation for soluble arsenic removals reported by all coagulation processes. Stable complexes of arsenate and arsenite form with most polyvalent metals, particularly iron, aluminium and zinc, and these complexes are captured by the hydroxide precipitation of these metals at the pH of metal hydroxide formation (Patterson, 1975).

A maximum of 40% reduction of arsenic (III) was obtained by activated carbon; however, the same was found to be suitable for removing arsenic (V). Lignite-based activated carbons were reported to be more suitable than bituminous coal-based activated

carbons in removing arsenic (V) from water (Huang and Fu, 1984). Removals upto 84% with powdered carbon and 61% with granular carbon were obtained at pH of 4.0.

Excellent removals of arsenic (V) on Fe^{2+} -treated activated carbon have also been reported (Huang and Vane, 1989). The formation of ferrous arsenate surface complexes, as opposed to the formation of coprecipitates in the bulk solution, was postulated as the mechanism of arsenic removal.

Chelating resins in the ferric iron form, Fe (III), effectively removed arsenic (III) and arsenic (V) from aqueous solution. Arsenic (III) removal is effective in the pH range of 8-11, whereas arsenic (V) can be removed in the pH range of 4-7. The mechanism of removal appears to be complexation between the immobile Fe (III) and arsenic. The resin is regenerated by stripping the complex with a dilute sodium hydroxide (NaOH) solution followed by reactivation with an Fe (III) solution at pH 0.8 (Chanda et al., 1988).

2.3 Iron Oxide-Coated Sand-An Adsorptive Filtration Medium

Removal of both cationic and anionic metals using adsorptive filtration by iron oxide-coated sand, proposed by Edwards and Benjamin (1989b), combines the advantages of the processes of adsorption and filtration. Amorphous iron oxide (ferrihydrite) is an excellent, regenerable adsorbent. In a laboratory study (Edwards and Benjamin, 1989a), ferrihydrite formed by reacting ferric nitrate and sodium hydroxide) was shown

to remove copper, cadmium, zinc, nickel and chromium from both synthetic and real metal-plating wastes to levels lower than that attainable by precipitation. Gullede and O'Connor (1973), achieved excellent arsenic (V) removal from water by adsorption on ferrihydrite. Edwards and Benjamin (1989b) developed methods of coating sand with iron oxide to produce an adsorbent with greater flexibility in application, combining the advantages of adsorption and filtration processes.

The iron oxide-coated sand outperformed uncoated sand in removing both uncomplexed and ammonia-complexed soluble metals. For a synthetic waste solution containing copper (3.2 mg/L), nickel (2.9 mg/L), trivalent chromium (2.6 mg/L), cadmium (2.8 mg/L) and lead (5.2 mg/L), almost complete removal of all metals (soluble) was observed in batch test at pH above 7.0; however, in the entire pH range studied (4.5-9.5), almost complete removal of trivalent chromium was observed. In a recent presentation, Benjamin and Sletten (1992) reported good removal (effluent levels less than 0.2 mg/L of total zinc and less than 0.1 mg/L of soluble zinc) of zinc from a treated (precipitation and settling at pH 8.0), zinc-bearing waste by iron oxide-coated sand. Bailey et al. (1992) have reported more than 99% removal of hexavalent chromium from a 20 mg/L synthetic waste solution by iron oxide-coated sand prepared by heating sand in presence of a precipitate formed by addition of sodium hydroxide to ferric nitrate solution.

Satpathy (1993) undertook a laboratory study to assess the suitability of iron oxide-coated sand for treatment of

metal-plating waste. Preliminary column studies indicated unsuitability of the medium for removal of chromium (2.5-2.6 mg/L). However, the medium appeared promising in removing cadmium (3.6-3.7 mg/L) and cyanide (0.85-0.95 mg/L) from the cadmium-plating waste. A detailed column test further indicated suitability of the medium in removing cadmium and cyanide. 90-100 bed volumes of cadmium-plating waste could be treated by the medium to meet the 1.0 mg/L tolerance limit of cadmium discharge of industrial waste into inland surface waters.

3. SCOPE OF THE PRESENT STUDY

From the preceding discussion it is evident that arsenic in water may be an acute problem in many areas where drinking water is primarily the groundwater. Effective methods of arsenic removal from groundwater include conventional water treatment involving coagulation followed by settling and filtration as well as point-of-use devices employing ion exchange, reverse osmosis, activated carbon, and activated alumina. However, these methods do not appear to be feasible for village-level application in a developing country, primarily due to their high cost and requirement of skilled operation. Simple, low-cost alternatives for removing arsenic from groundwater need to be developed. Recently, iron oxide-coated sand in fixed-bed has been successfully employed in several laboratory studies to treat metal-bearing wastewaters. The spent medium is regenerated by washing with an acidic/alkaline solution. Promisingly, this method may be adapted to provide a simple means of removing arsenic from groundwater. Consequently, the present study was undertaken to assess the suitability of iron oxide-coated sand for removal of arsenic (III) and arsenic (V) from groundwater with a view to its use as a medium in a home arsenic removal unit. Notably, the 1993 Inorganic Contaminants Research Committee of the American Water Works Association has identified studies on the possible removal of arsenic using iron oxide-coated sand in fixed-bed columns as one of the current research needs (Committee Report, 1993). The study was conducted along the following lines :

- a. Subjecting iron oxide-coated sand to batch arsenic sorption kinetic test.
- b. Several cycles of downflow column test to investigate the practical aspects of arsenic removal from groundwater by iron oxide-coated sand *vis-à-vis* its use as a medium in home arsenic removal units.
- c. Development of a home arsenic removal unit and evaluating its performance.

4. MATERIALS AND METHODS

4.1 Arsenic-Bearing Water

Water used in the study was I.I.T., Kanpur tap water (a direct groundwater supply). A typical analysis of the water is presented in Table 1. The water was spiked with 1.0 mg arsenic (III)/L using sodium arsenite (NaAsO_2) or 1.0 mg arsenic (V)/L using sodium arsenate (Na_2HAsO_4) for use in batch arsenic sorption kinetic test, column test and home arsenic removal unit performance evaluation.

Table 1. Analysis of I.I.T., Kanpur Tap Water

pH	7.5 \pm 0.1
Alkalinity, mg/L as CaCO_3	400
Hardness, mg/L as CaCO_3	180
Calcium, mg/L as CaCO_3	60
Magnesium, mg/L as CaCO_3	97
Conductivity, $\mu\text{mhos/cm}$	5.5×10^{-4} at 22 °C
Arsenic, mg/L	Not detected

4.2 Determination of Arsenic

Many methods are available for estimation of arsenic in water but most of them are either unsuitable or tedious for quantitative determination of arsenic at low concentration. To overcome this problem, arsenic was determined by Johnson's spectrophotometric method (Johnson and Pilson, 1972). This method

allows for routine analysis of arsenite, arsenate, and phosphate by spectrophotometric measurement of the arsenic and phosphate molybdenum blue complexes. A reducing reagent^a is used to lower the oxidation state of any arsenic present to +3, which eliminates any absorbance caused by molybdoarsenate, since arsenite will not form the molybdenum complex. This results in an absorbance value for phosphate only. The mixed reagent^b added to an "untreated" sample produces a colour from both molybdophosphate and molybdoarsenate formed from any arsenate present. The difference between the two absorbance readings, when corrected for suitable blanks, is proportional to the arsenate concentration. In this method, potassium iodate is used as an oxidizing agent to convert arsenite to arsenate; suitable experimental conditions have been established so that the difference between an "oxidized" and a "reduced" sample is the absorbance arising from total inorganic arsenic. Arsenite is then calculated as the difference between total arsenic and arsenate arsenic.

As Johnson's spectrophotometric method is for duplicate analysis, each sample was analysed in duplicate. In the

^aReducing reagent (Johnson, 1971) : 20 mL of 3.5N sulphuric acid was added to 40 mL of 0.74M sodium metabisulphite solution and mixed thoroughly. Finally, 40 mL of 0.056M sodium thiosulfate solution was added to it, with thorough mixing. If refrigerated, the reducing reagent is stable for upto 24 hours.

^bMixed reagent (Murphy and Riley, 1962) : 125 mL of 5N sulphuric acid and 37.5 mL of 0.032M ammonium molybdate solution were mixed thoroughly. Then 75 mL of 0.1M ascorbic acid solution and 12.5 mL of 0.0082M potassium antimonyl tartrate solution were added successively, with through mixing after each addition. This reagent is to be prepared as required as it does not keep for more than 24 hours.

procedure, 40 mL of the sample was taken into each of six 125 mL Erlenmeyer flasks. Two flasks were for "oxidized" aliquots, two for the "reduced", and two for the "untreated" aliquots. 1 mL of 1N hydrochloric acid and one drop of the 50% saturated potassium iodate solution were added successively, to each of the "oxidized" aliquots, with thorough mixing after each addition. Two minutes were allowed for oxidation of arsenite to arsenate. Thereafter, 4 mL of the mixed reagent was added to each of the "oxidized" and the "untreated" sample aliquots with thorough mixing. This was followed by successive addition of one drop of the iodate solution and 1 mL of 1N hydrochloric acid to each of the "untreated" aliquots with thorough mixing after each addition. Colour formation in the "oxidized" and "untreated" aliquots was allowed to take place for 4 hours, following which absorbances were read in a 1 inch cell at a wavelength of 865 nm.

For clarity, the treatment of the "reduced" aliquots is described separately below, though in practice they were run concurrently with the "oxidized" and the "untreated" aliquots. The reducing reagent (4 mL) was added to the "reduced" aliquots after thorough mixing. The "reduced" aliquots were allowed to react for 3 hours for reduction of arsenate to arsenite. Thereafter, the mixed reagent (4 mL) was added to the "reduced" aliquots with thorough mixing. Colour formation was allowed to take place for 15 minutes following which the absorbances were read as described above.

Blanks were run, by the above procedures, alongwith the samples. Since the final volume of the "reduced" aliquots was greater than that of the other aliquots, a dilution correction was made to obtain corrected absorbances (C.A.).

$$\text{arsenite} = (\text{C.A. "oxidized"} - \text{C.A. "untreated"})$$

$$\text{arsenate} = (\text{C.A. "untreated"} - \text{C.A. "reduced"})$$

Calibration curves for arsenite, arsenic (III), and arsenate, arsenic (V), were prepared and are shown in Fig. 1 and Fig. 2, respectively.

4.3 Preparation of Iron Oxide-Coated Sand

River sand passing through 800 μm and retained on 300 μm sieves was used. The sand was washed and dried at 105 $^{\circ}\text{C}$ before the oxide coating was applied. A method suggested by Bailey et al. (1992) was employed for coating sand with iron oxide. Sand (200 g) and 80 mL of a 2M ferric nitrate solution (adjusted to a pH of 11.0 with sodium hydroxide) were mixed for 2 minutes. Thereafter, the mixture was placed in a 110 $^{\circ}\text{C}$ drying oven for 14 hours. The coated sand was then washed with distilled water until the runoff was clear, dried at 35 $^{\circ}\text{C}$, and stored in capped bottles until used.

Satpathy (1993) characterised the iron oxide-coated sand thus prepared. Microscopic examination of the iron oxide-coated sand showed that the coating was rather patchy even though it appeared fairly uniform to the naked eye. Surface area of the coated sand, measured in a Micrometrics Pulse Chemisorb 2000

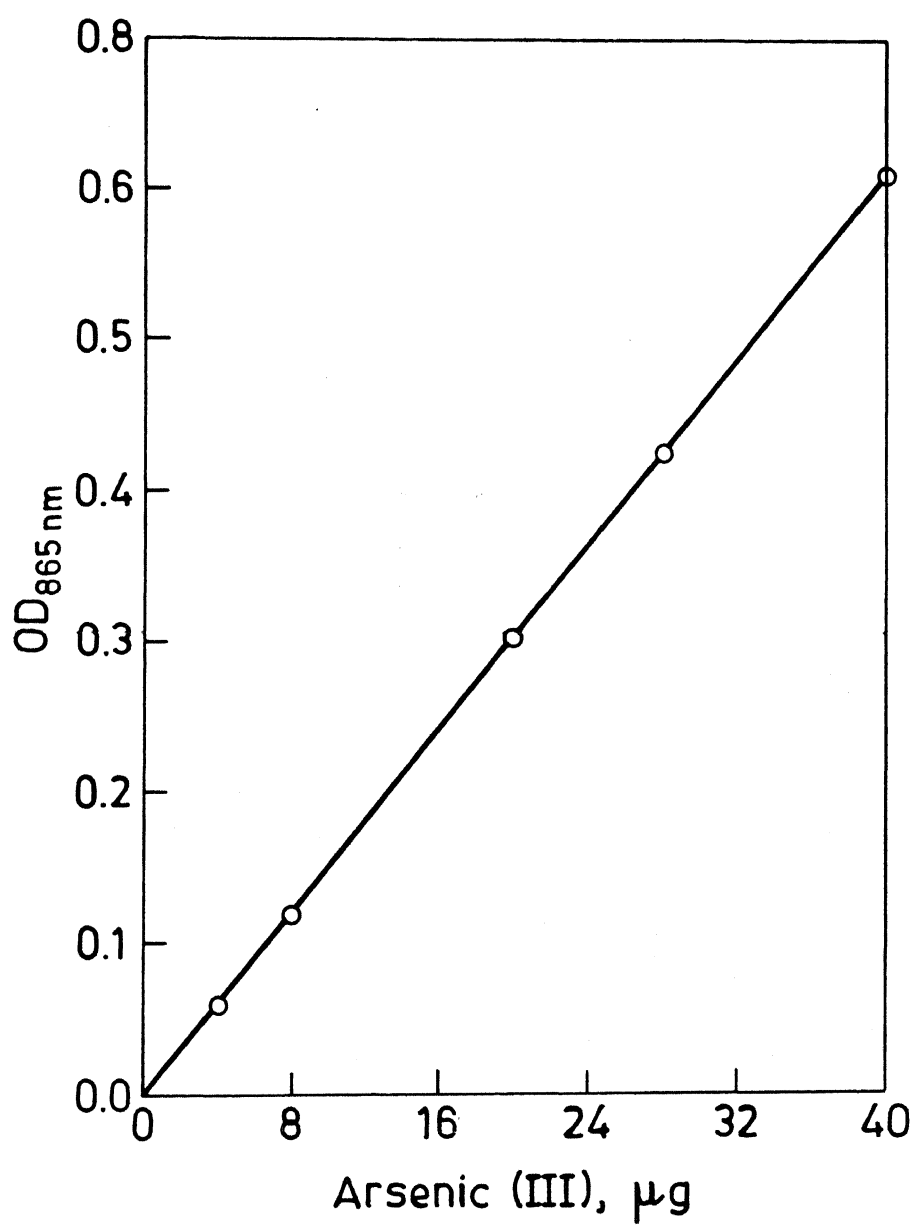


Fig. 1. Calibration curve for arsenic (III).

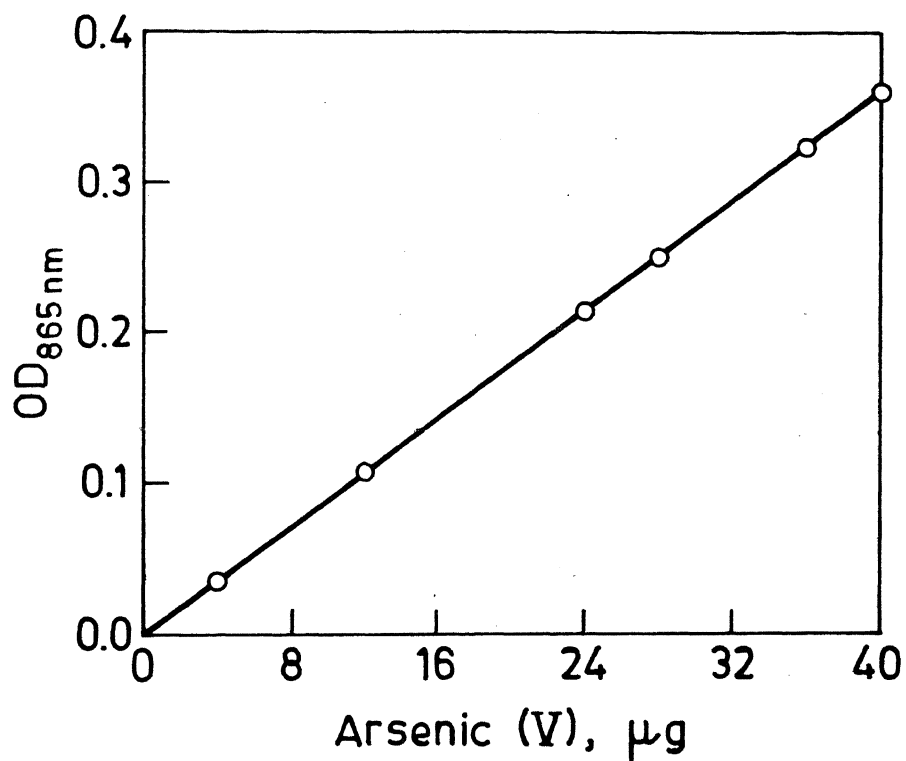


Fig. 2. Calibration curve for arsenic (V).

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instrument, was $1.59 \text{ m}^2/\text{g}$ compared to $0.039 \text{ m}^2/\text{g}$ for the uncoated sand, indicating a fortyfold increase in surface area as a result of coating. Based on fast alkalimetric titration, the pH of zero point charge of the coated sand was found to be 9.0.

4.4 Arsenic Sorption Kinetic Test

Batch sorption kinetic test was conducted separately for arsenic (III) and arsenic (V), using iron oxide-coated sand and uncoated sand as sorbents. The arsenic-bearing water (250 mL) and 2.5 g of a sorbent (10 g/L) in 300 mL glass bottles were placed in an end-over-end shaker at 20 rpm. At predetermined contact times ($\frac{1}{2}$, 1, 2, 3, 4, 6, 8 and 12 hours), duplicate bottles were withdrawn, the sorbent separated by settling (10 minutes) and the supernatant analysed for residual arsenic.

4.5 Column Test

Two parallel downflow column tests were conducted for removal of arsenic (III) and arsenic (V) using the arsenic-bearing water (1.0 mg arsenic (III)/L or 1.0 mg arsenic (V)/L). Each 1.1 cm ID glass column was packed with 50 mL (75 g) of iron oxide-coated sand (60 cm medium depth) and backwashed with distilled water to remove any particulates. A flow rate of 1.0 mL/min, yielding a bed flowthrough time of 50 minutes was used. Column runs were continued until effluent arsenic exceeded the WHO guideline value (0.01 mg/L) for arsenic in drinking water. Following termination of a run, the medium was regenerated *in situ* by backwashing with 2 L of a 0.2N sodium hydroxide solution. The

column was then equilibrated by circulating distilled water until the influent and effluent pH were identical.

The spent regenerant and backwash water were collected for ten cycles of operation and analysed for recovered arsenic. Using the data, a column loading-regeneration material balance was made in terms of the amount of arsenic on the coated sand subjected to regeneration (arsenic picked up by the coated sand in column run in addition to that remaining from the preceding cycle) and the amount of arsenic recovered in regeneration.

5. RESULTS AND DISCUSSION

Results of all experiments are presented in graphical form followed by a discussion of each phase of the experimental work. Majority of experiments were performed in duplicate and the typical results are reported.

5.1 Arsenic Sorption Kinetic Test

Using the arsenic-bearing water (arsenic (III) 1.0 mg/L or arsenic (V) 1.0 mg/L), separate sorption kinetic tests were conducted to ascertain the time required for equilibrium arsenic (III) or arsenic (V) sorption by the iron oxide-coated sand. For arsenic (III), equilibrium sorption (76%) was attained in 4 hours while for arsenic (V), equilibrium sorption (83%) was attained in 8 hours (Fig. 3). About 60% sorption of arsenic (III) or arsenic (V) occurred in one hour. Uncoated sand showed very little sorption (5-10%) of arsenic (III) or arsenic (V). The results indicated suitability of the iron oxide-coated sand in removing both arsenic (III) and arsenic (V) from groundwater.

5.2 Column Test

Ten cycles of downflow column tests, using 50 mL (75 g) of iron oxide-coated sand in a 1.1 cm ID glass column (60 cm medium depth) and a flow rate of 1.0 mL/minute (bed flowthrough time 50 minutes) were conducted to assess the potential of iron oxide-coated sand for use in home arsenic removal units for removal of arsenic (III) or arsenic (V) from groundwater.

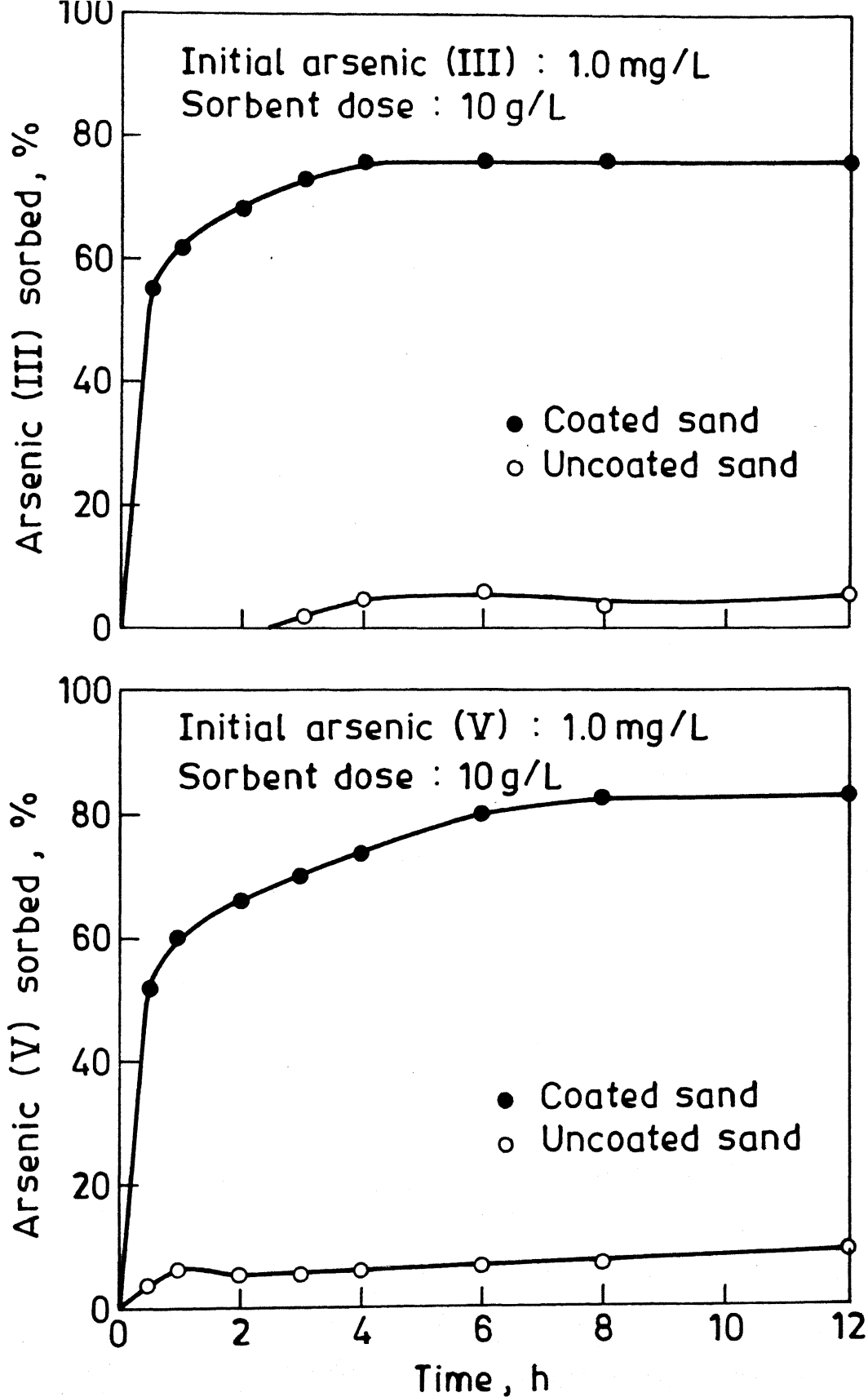


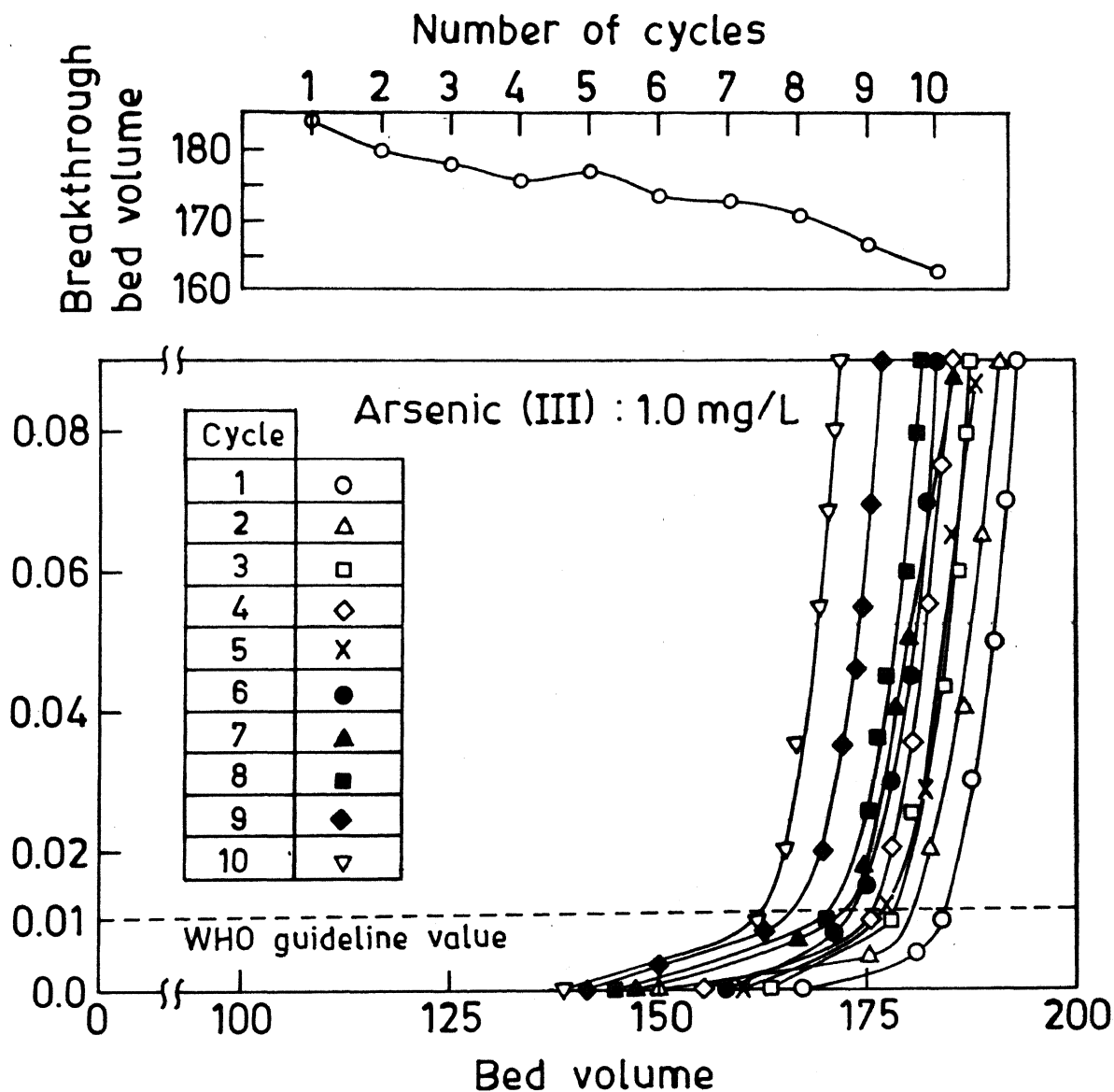
Fig. 3. Kinetics of arsenic sorption on uncoated and iron oxide-coated sand.

On the basis of the arsenic sorption kinetic test data (Fig. 3), equilibrium for arsenic (III) or arsenic (V) sorption was attained at a contact time of 4 or 8 hours. For a contact time of one hour, arsenic (III) or arsenic (V) sorption was about 60% . Any home treatment device has to have a flowthrough time so that appreciable amount of water can be treated in an hour. A flowthrough time of 50 minutes was selected for the column test keeping the above factor in mind.

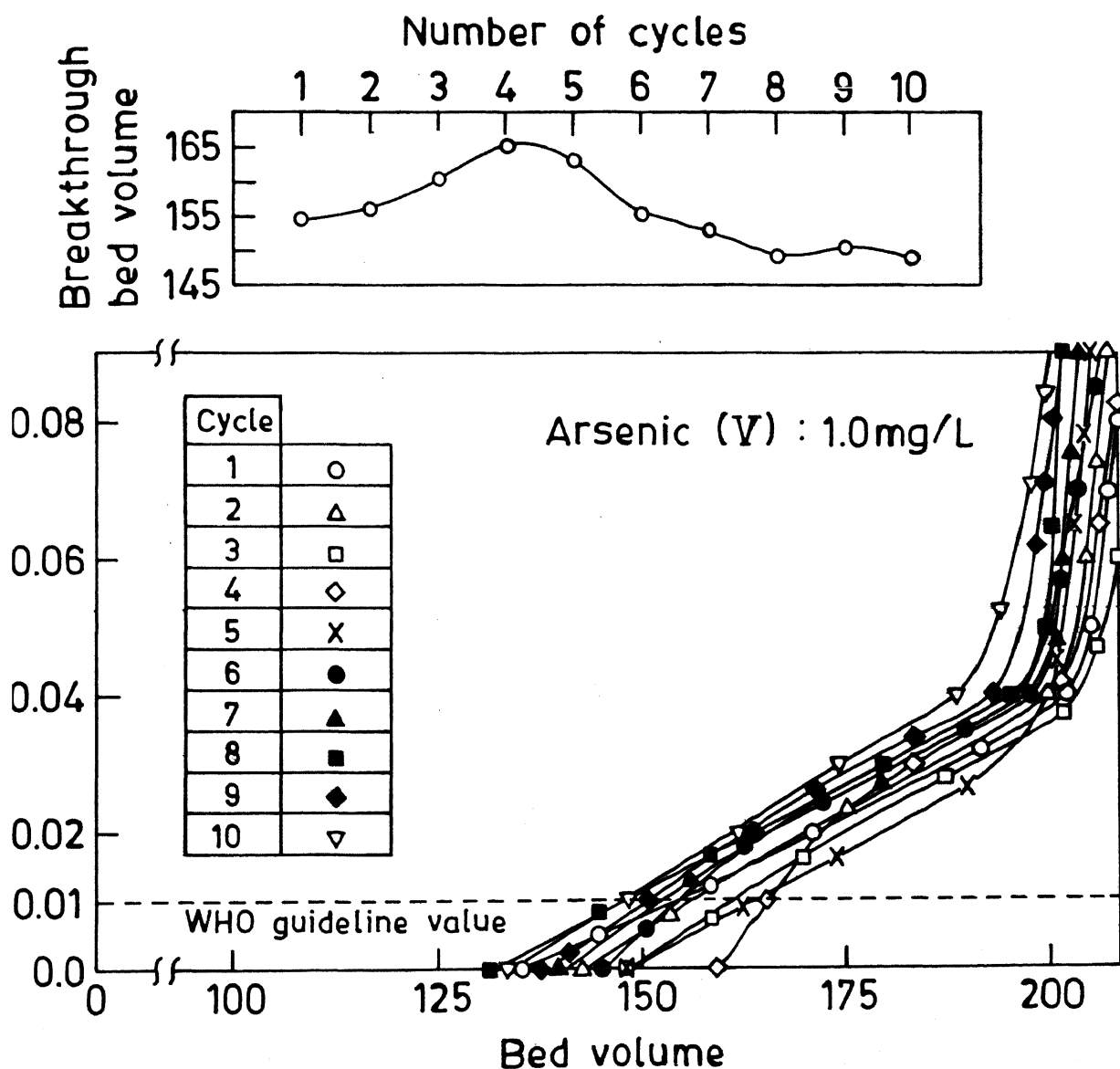
Arsenic (III) and arsenic (V) removal in ten cycles of column test is shown in Fig. 4 and 5, respectively. Breakthrough bed volumes at the WHO guideline value (0.01 mg/L) for arsenic in drinking water were in the range 163-184 per cycle for arsenic (III) and 149-165 per cycle for arsenic (V). The results of the column test indicated suitability of the iron oxide-coated sand for use as a medium in a home arsenic removal unit.

Column loading-regeneration material balance for arsenic (III) and arsenic (V) shown in Tables 2 and 3, respectively indicated further the suitability of iron oxide-coated sand for use as a medium in a home arsenic removal unit.

Even though a detailed study on regeneration of arsenic-loaded iron oxide-coated sand and a probe into the difference in its arsenic (III) and arsenic (V) removal capacities (as observed in the column test) are called for, it was considered appropriate at this stage to fabricate iron oxide-coated sand-based home



4. Performance of iron oxide-coated sand in arsenic (III) removal in ten cycles of column test.



5. Performance of iron oxide-coated sand in arsenic (V) removal in ten cycles of column test.

Table 2. Column loading-regeneration material balance for arsenic (III)

	Number of cycles									
	1	2	3	4	5	6	7	8	9	10
Arsenic (III) from Preceding cycle, µg/g	0	28.8	23.36	31.18	32.55	37.24	41.08	40.2	43.5	50.26
Arsenic (III) picked up in column run, µg/g	150.0	146.67	133.33	125.33	126.0	122.67	122.67	121.33	120.0	117.33
Arsenic (III) on coated sand subjected to regeneration, µg/g	150.0	175.47	156.69	156.51	158.55	159.91	163.75	161.53	163.5	167.59
Arsenic (III) recovered in regeneration, µg/g	121.2	152.11	125.51	123.96	121.31	118.83	123.55	118.03	113.24	113.98
Arsenic (III) remaining on coated sand, µg/g	28.8	23.36	31.18	32.55	37.24	41.08	40.2	43.5	50.26	53.61
Recovery of arsenic (III), %	80.8	86.69	80.1	79.2	76.51	74.31	75.45	73.07	69.26	68.01

Table 3. Column loading-regeneration material balance for arsenic (V)

	Number of cycles									
	1	2	3	4	5	6	7	8	9	10
Arsenic (V) from preceding cycle, $\mu\text{g/g}$	0	3.55	2.78	5.02	11.88	16.29	13.26	17.56	23.21	28.75
Arsenic (V) picked up in column run, $\mu\text{g/g}$	152.48	154.31	141.33	144.0	138.67	137.33	139.33	138.0	136.0	136.67
Arsenic (V) on coated sand subjected to regeneration, $\mu\text{g/g}$	152.48	157.86	144.11	149.02	150.55	153.62	152.59	155.56	159.21	165.42
Arsenic (V) recovered in regeneration, $\mu\text{g/g}$	148.93	155.08	139.09	137.14	134.26	140.36	135.03	132.35	130.46	132.78
Arsenic (V) remaining on coated sand, $\mu\text{g/g}$	3.55	2.78	5.02	11.88	16.29	13.26	17.56	23.21	28.75	32.64
Recovery of arsenic (V), %	97.67	98.24	96.52	92.03	89.18	91.37	88.49	85.08	81.94	80.27

arsenic removal units and evaluate their performance in removing arsenic (III) and arsenic (V) from groundwater.

6. HOME ARSENIC REMOVAL UNIT

Two identical home arsenic removal units were fabricated using galvanised iron sheet to study arsenic (III) and arsenic (V) removal (Fig. 6). A unit consists of two chambers, placed one above the other. The top chamber (38 cm x 20 cm ID) holds 4 L (6 Kg) of iron oxide-coated sand medium up to a height of 15 cm and serves as the raw water reservoir. The bottom chamber (28 cm x 20 cm ID) is fitted with a tap and serves as a storage for the treated water. A brass disc with a 1.5 mm diameter orifice is fitted to the bottom chamber to produce a flow rate of 6 L/h. This provides a bed flowthrough time of 40 minutes.

In each run, 7 L of arsenic-bearing water (arsenic (III) 1.0 mg/L or arsenic (V) 1.0 mg/L) were placed in the top chamber and allowed to pass completely into the bottom chamber. Ten runs were conducted daily till the effluent arsenic exceeded the WHO guideline value (0.01 mg/L) for arsenic in drinking water. This constituted one cycle. Following this, the medium was regenerated *in situ* using 10 L of 0.2 N sodium hydroxide followed by washing with 10 L of water, and a second cycle was conducted in a similar manner. Periodic sampling of the effluent during regeneration indicated that 10 L was an adequate volume for maximum possible regeneration.

The unit produced 625 L of effluent with arsenic (III) level below the WHO guideline value (0.01 mg/L) for arsenic in drinking water in the first cycle (Fig. 7). A total of 79.61% of arsenic (III) removed was recovered during regeneration. The

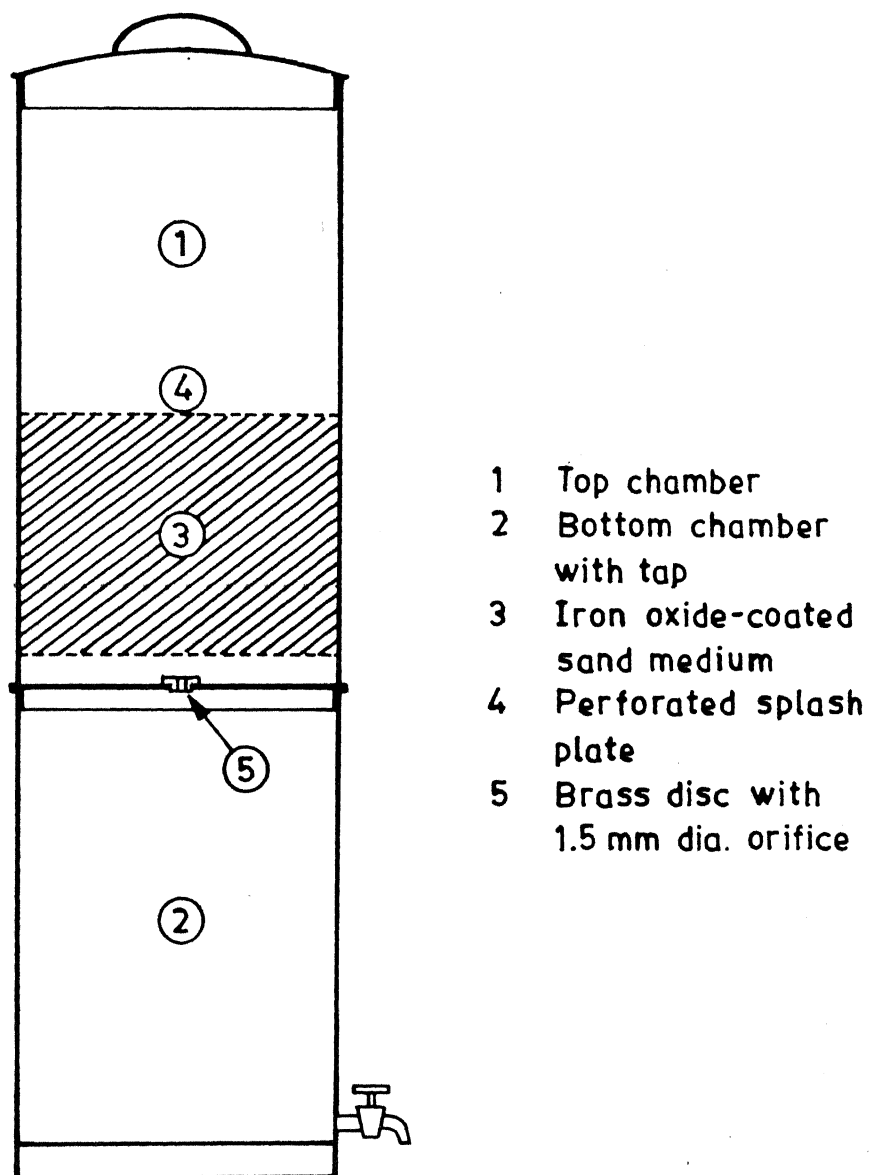


Fig. 6. Home arsenic removal unit.

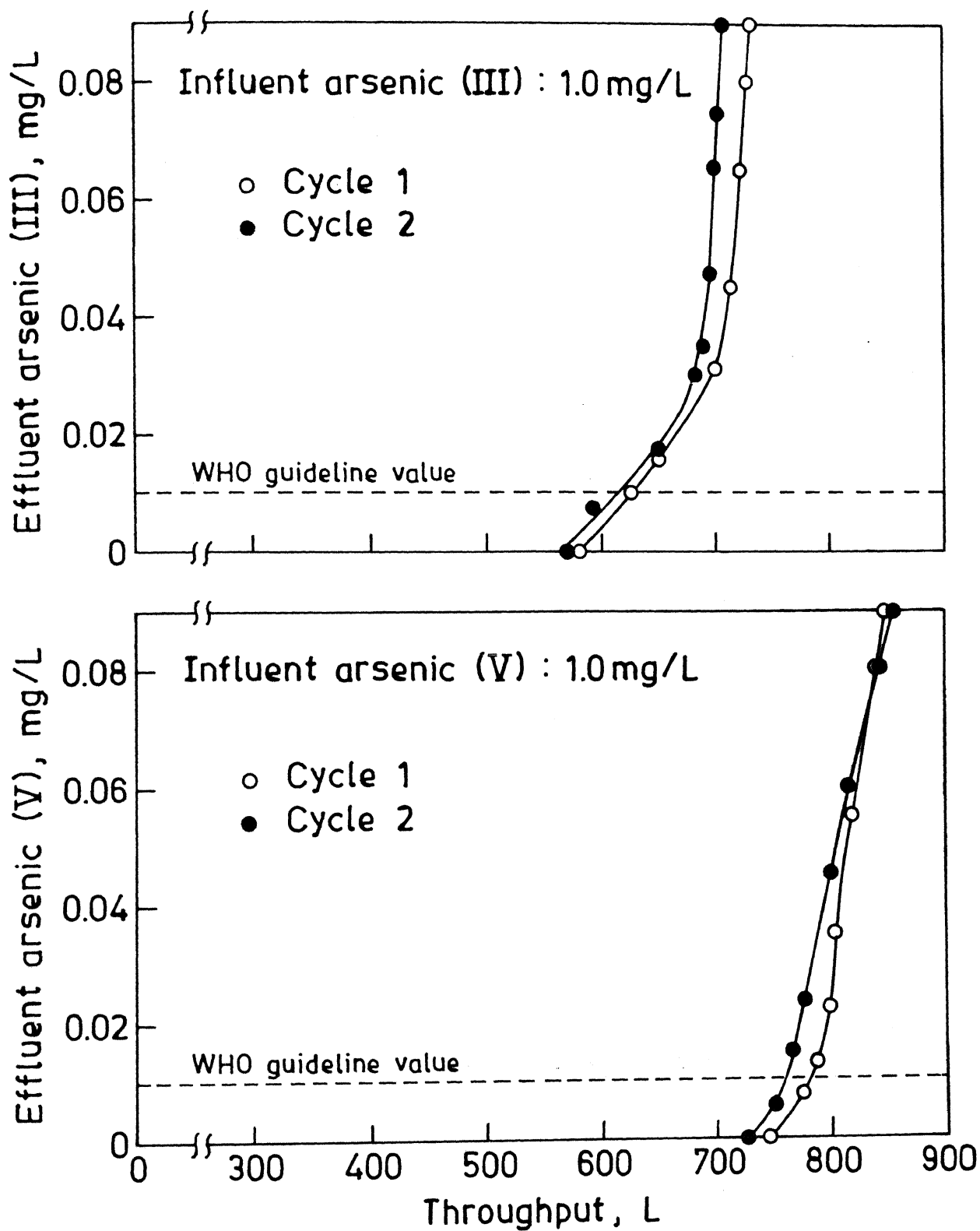


Fig. 7. Performance of home arsenic removal unit.

second cycle produced 610 L of effluent. For arsenic (V), the two cycles produced 780 and 760 L of effluent. A total of 96.74% of arsenic (V) removed was recovered during regeneration.

Performance of the iron oxide-coated sand-based home arsenic removal unit was quite encouraging in removing arsenic (III) and arsenic (V) from groundwater. However, the unit needs to be tested using natural arsenic-bearing waters containing both arsenic (III) and arsenic (V).

7. SUMMARY AND SUGGESTIONS

Iron oxide-coated sand, subjected to batch arsenic sorption kinetic test using an arsenic-spiked groundwater (arsenic (III) 1.0 mg/L or arsenic (V) 1.0 mg/L), showed 76% arsenic (III) sorption and 83% arsenic (V) sorption at 10 g/L sorbent dose in 4 and 8 hours, respectively. Uncoated sand showed very little (5-10%) arsenic sorption. Ten cycles of downflow column tests, using 50 mL (75 g) of iron oxide-coated sand in a 1.1 cm ID glass column (60 cm medium depth) and a flow rate of 1.0 mL/min (bed flowthrough time 50 minutes) were conducted to assess the potential of iron oxide-coated sand for use in home arsenic removal units for removal of arsenic (III) or arsenic (V) from groundwater. Breakthrough bed volumes at the WHO guideline value (0.01 mg/L) for arsenic in drinking water were in the range 163-184 per cycle for arsenic (III) and 149-165 per cycle for arsenic (V). A home arsenic removal unit containing 4 L (6 kg) of iron oxide-coated sand and operated at 6 L/h produced 625 and 610 L of effluent with arsenic (III) level below the WHO guideline value (0.01 mg/L) for arsenic in drinking water in two successive cycles. An identical unit produced 780 and 760 L of effluent with arsenic (V) level below the WHO guideline value (0.01 mg/L) for arsenic in drinking water in two successive cycles.

A study to evolve a more cost-effective regeneration procedure and testing the home arsenic removal unit using natural

arsenic-bearing waters are suggested. It is also recommended that the unit be field-tested in one of the affected areas in West Bengal and its performance monitored to evolve better design and operational criteria.

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